

## LA-UR-17-28232

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Title: Doped-UO<sub>2</sub> Advanced Technology Fuel

Author(s): Stanek, Christopher Richard

Intended for: Discussions with relevant industry stakeholders

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# Doped $\text{UO}_2$ Advanced Technology Fuel

Chris Stanek

# Motivation

## $\text{Cr}_2\text{O}_3$ Doped $\text{UO}_2$ Fuel, BWR Implementation

AREVA/NRC  
Rockville, MD  
June 25, 2015

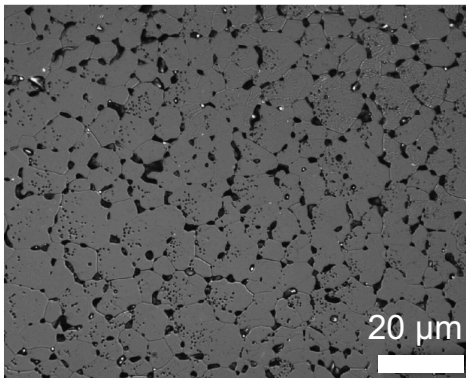
## Background

- ▶  $\text{Cr}_2\text{O}_3$ -doped fuel is standard  $\text{UO}_2$  with  $\text{Cr}_2\text{O}_3$  added at a level, which is above the ASTM impurity level allowed for Cr (~ 250 ppm)
- ▶  $\text{Cr}_2\text{O}_3$  addition has a significant impact on  $\text{UO}_2$  microstructure: increased grain size with the dopant principally dissolved in the  $\text{UO}_2$  matrix
- ▶ The  $\text{Cr}_2\text{O}_3$ -doped fuel has enhanced fission product retention and enhanced viscoplasticity, leading to:
  - ◇ Lower fission gas release, especially during transients
  - ◇ Enhanced pellet creep with benefits in operational maneuvers

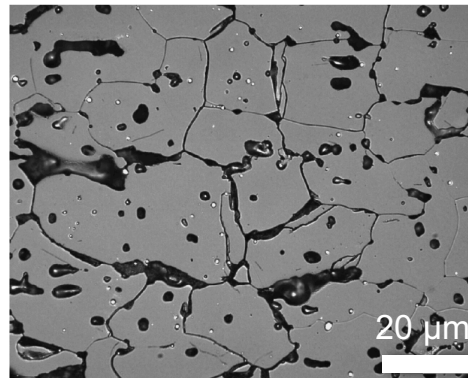


# Background

Undoped  $\text{UO}_2$



Cr (1000ppm)  
doped  $\text{UO}_2$



- Cr-doped  $\text{UO}_2$  exhibits larger grains
  - 4-5 times increase in grain size when doped with 1000 ppm Cr
- Al-doped  $\text{UO}_2$  does not exhibit enhanced grain size
- Combination of Cr and Al shows even larger enhancement

Pellet segments	Pellet composition	Density (%/(g/cm <sup>3</sup> ))	3D grain size <sup>a)</sup> (μm)	<sup>235</sup> U enrichment (%)
Standard (Std)	$\text{UO}_2$	96.0/10.52	10–12	2.8 and 1.7
Standard Optima2 (Std Opt2)	$\text{UO}_2$	96.7/10.60	10–12	4.2
Doped $\text{UO}_2$ #1 (D1)	$\text{UO}_2$ +1,000 ppm $\text{Cr}_2\text{O}_3$	97.3/10.66	44 <sup>b)</sup>	4.2
Doped $\text{UO}_2$ #2 (D2)	$\text{UO}_2$ +1,000 ppm $\text{Cr}_2\text{O}_3$ +100 ppm MgO	97.4/10.68	42	4.2
Doped $\text{UO}_2$ #3 (D3)	$\text{UO}_2$ +500 ppm $\text{Cr}_2\text{O}_3$ +200 ppm $\text{Al}_2\text{O}_3$	97.4/10.68	52	4.2

Aborelius *et al.* *J. Nucl. Sci. Tech.* **43** 967-976 (2006)

# Motivation for atomistic simulation of doped $\text{UO}_2$

□ Multiple maxima in peak in grain size around solubility limit indicates complex sintering mechanistics

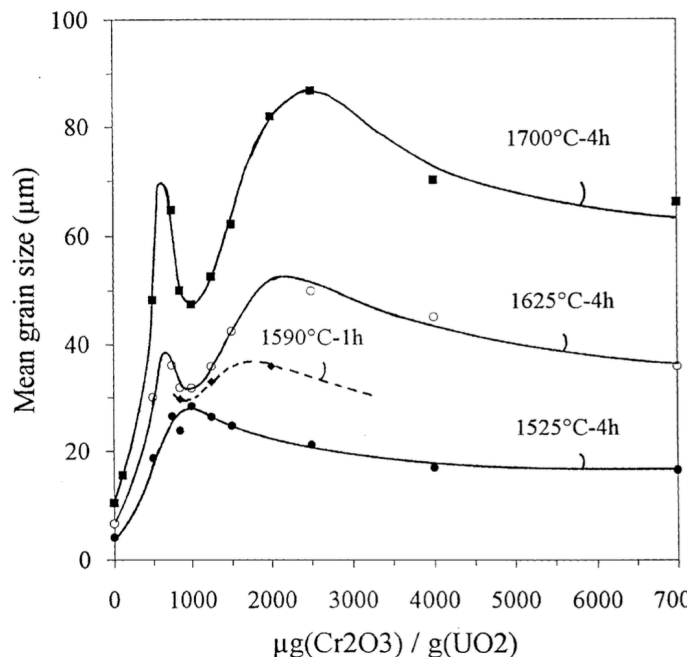
□ Industrial Cr-doped fuel concepts are at solubility limit – suggesting liquid phase sintering (which has been stated to govern the enhanced sintering) may not be only explanation

□ Approach is to thoroughly (re-)investigate Cr solution in  $\text{UO}_2$  as a function of charge state (note Cr can occupy 2+, 3+, 4+, 5+ and 6+ valence states).

□ **Two important potential implications of this study. Complete understanding of Cr defect physics will permit:**

□ *(1) optimized doping procedures.*

□ *(2) development of predictive fuel performance models (e.g. fission gas release).*



Bourgeois *et al.* *J. Nucl. Mater.* **297** 313-326 (2001)

# Possible mechanisms for enhanced sintering

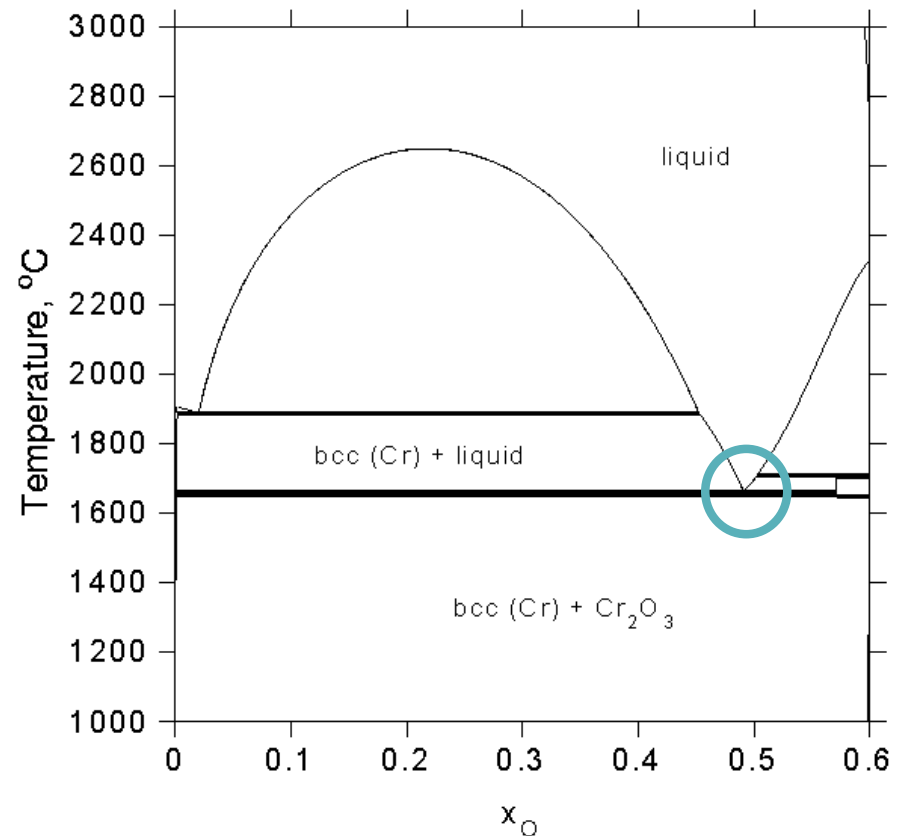
## Liquid phase sintering

If **Cr is insoluble** can it form oxide precipitates that are liquid at sintering temperatures (1900 K) and assist mass transport?

CrO system has a liquid eutectic

CrUO<sub>4</sub> may also form and might have a lower melting point

**But at 1000ppm Cr, volume fraction ~0.1 % -> seems small and this is also close to the solubility limit for Cr**



# Possible mechanisms for enhanced sintering

## Liquid phase sintering

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**But at 1000ppm Cr, volume fraction ~0.1 % -> seems small and this is also close to the solubility limit for Cr**

## Can Cr dissolve into UO<sub>2</sub> and increase the U vacancy concentration?

Uranium mass transport is the rate limiting step but is greatly increased by presence of U defects

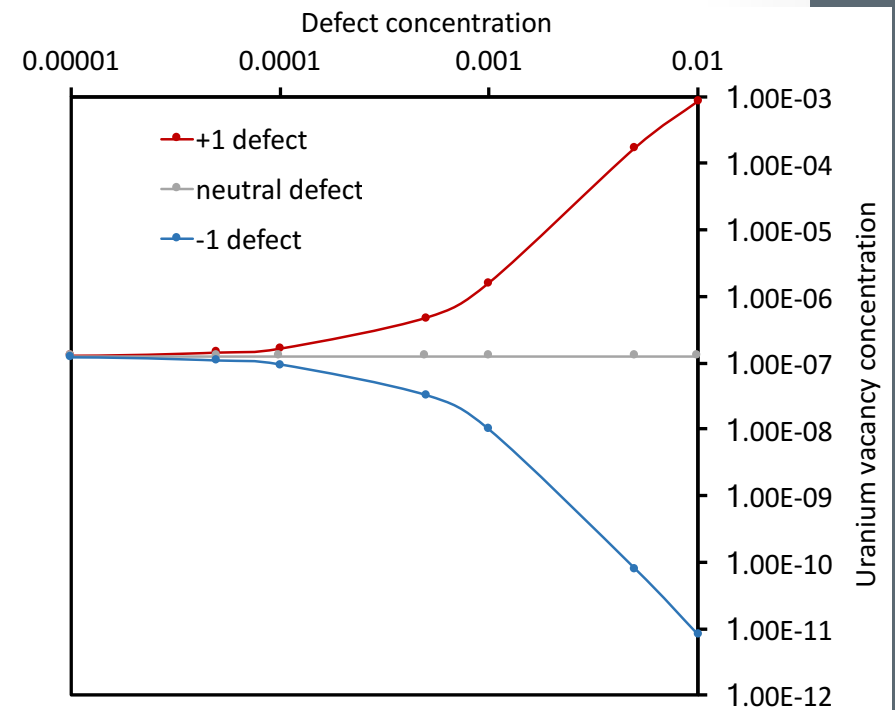
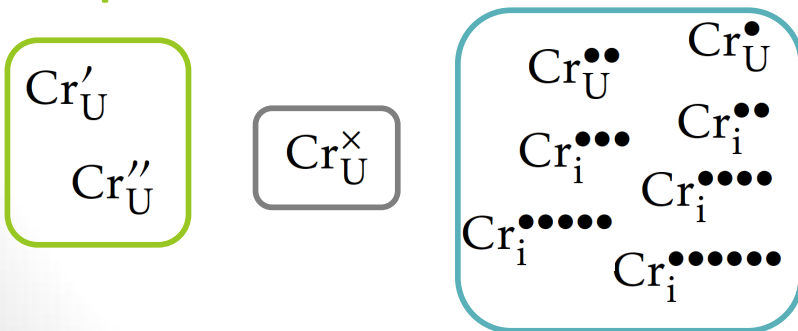
We need a high enough Cr solubility limit and the right type of Cr defects

Some Cr defects have not been considered in past work, meaning this mechanism should be further studied

# Uranium defects are key to enhanced mass transport and sintering

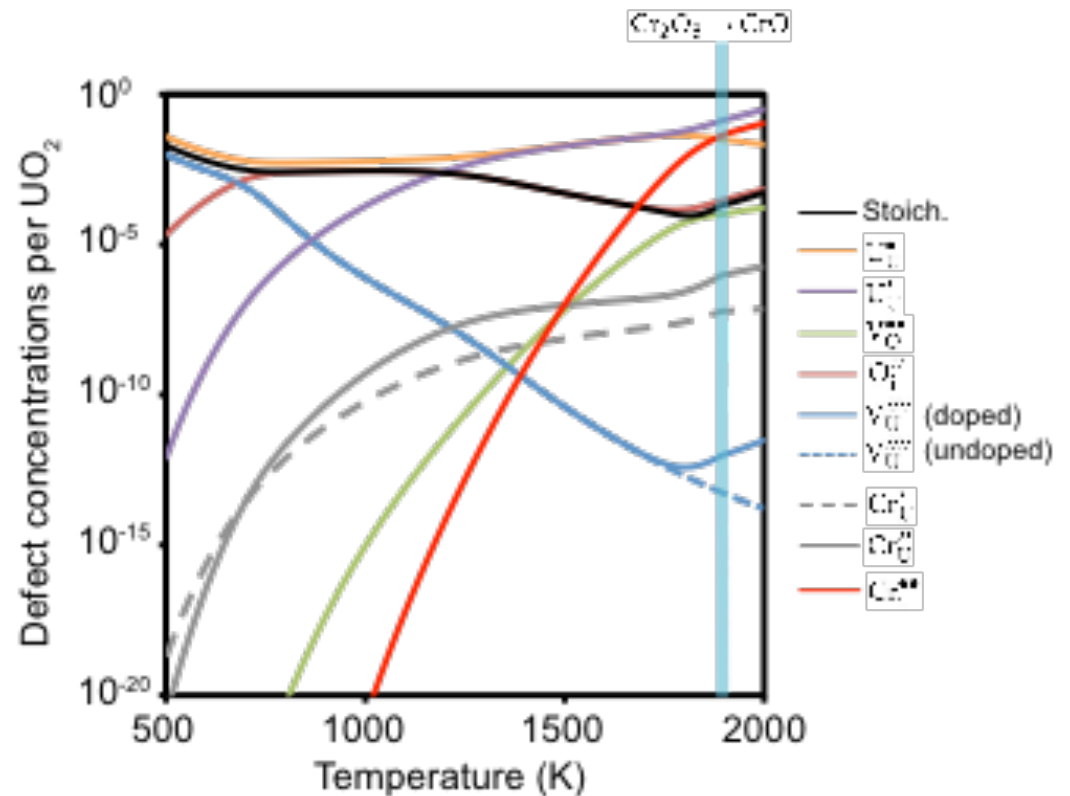
- U vacancy concentrations are key to U mass transport
- U vacancies are negatively charged defects
- If Cr solution is charge compensated by negatively charged defects, then U vacancy concentration is **suppressed**
- If Cr solution is charge compensated by positively charged defects, then U vacancy concentration is **enhanced**.

Options =



# Cr-doped $\text{UO}_2$ Results

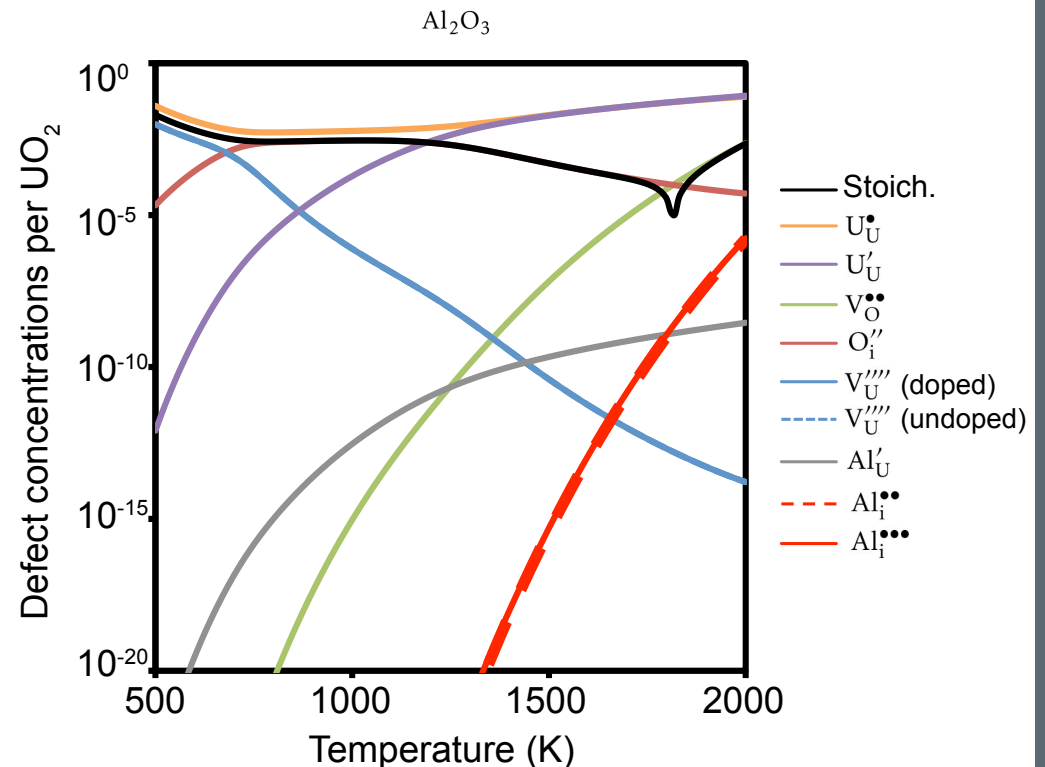
- DFT results indicate that at low temperatures very low Cr solubility at substitutional sites
  - Cr forms a negative defect at substitutional sites but negligible concentrations
- At high temperature vibrational entropy drives solubility onto the interstitial site
  - Significant concentrations of 2+ interstitial at sintering temperatures ( $>1700$  K)
- Outer shell has 5  $d$  electrons allowing multiple valence states



**Limiting consideration to  $\text{Cr}^{3+}$  or ignoring vibrational entropy will not capture role of Cr-doping**

# Al-doped $\text{UO}_2$

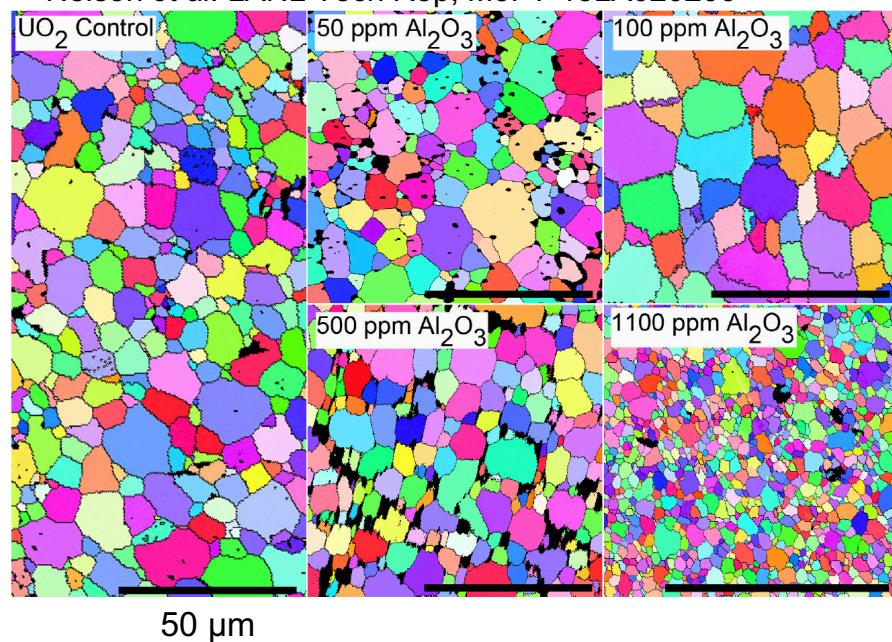
- ❑ Lower Al solubility than for Cr across full temperature range
- ❑ Seems that the interstitial necessitates the 2+ valence state
- ❑ Although  $\text{Al}_i^{\bullet\bullet}$  defect forms at high temperature it is still very insoluble so little impact on  $V_U$
- ❑ Insolubility of  $\text{Al}_i^{\bullet\bullet}$  is probably do to its electronic structure  $\rightarrow$  outer shell of  $s2p1$  so it strongly prefers +3 valence



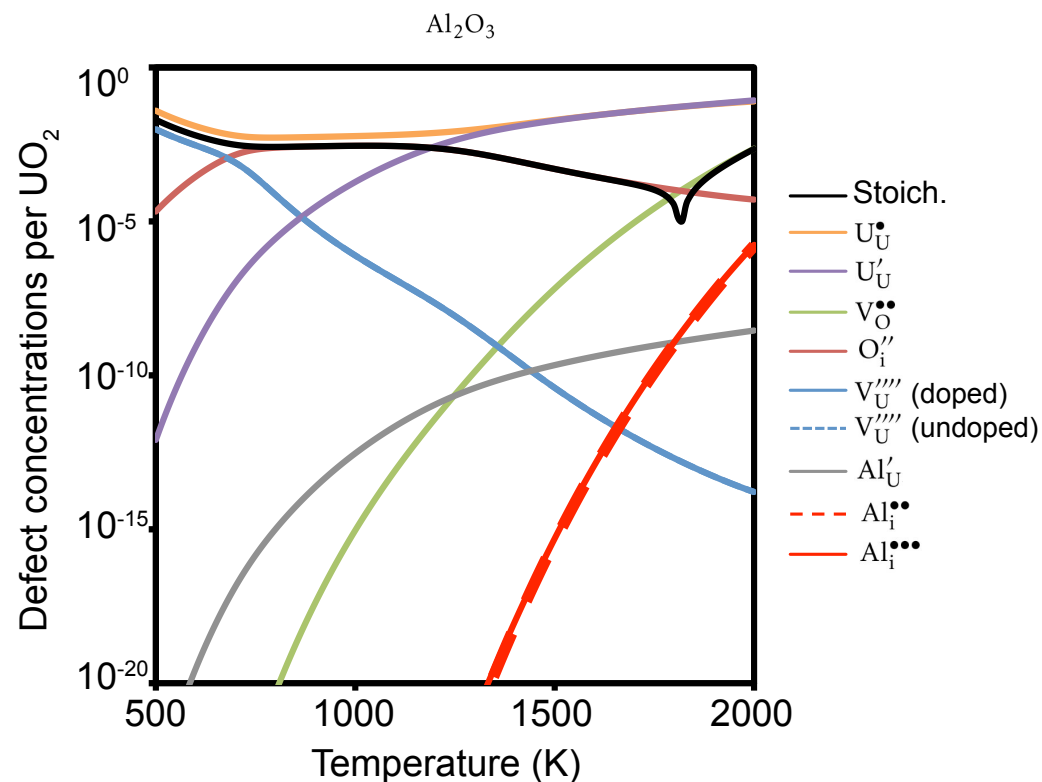


# Al-doped $\text{UO}_2$

Nelson *et al.* LANL Tech Rep, M3FT-13LA020206



- Past experimental work at LANL also showed no enhancement due to Al





# Ability to access 2+ valence state is key.

## Any other element that could be used as a sintering aid?

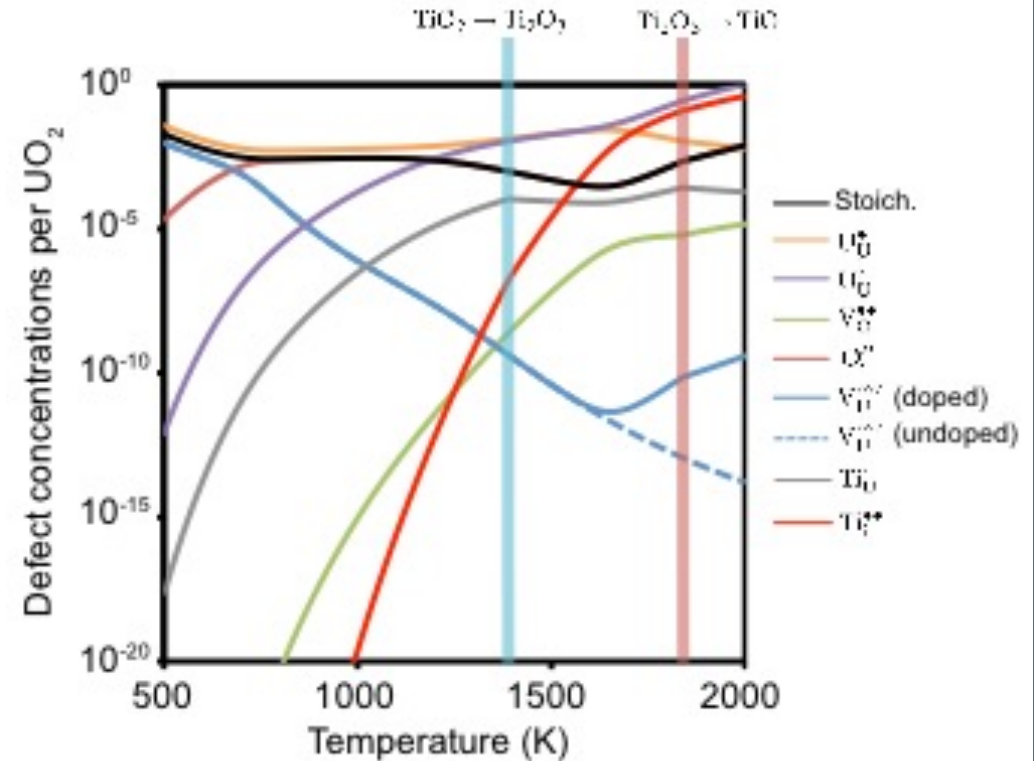
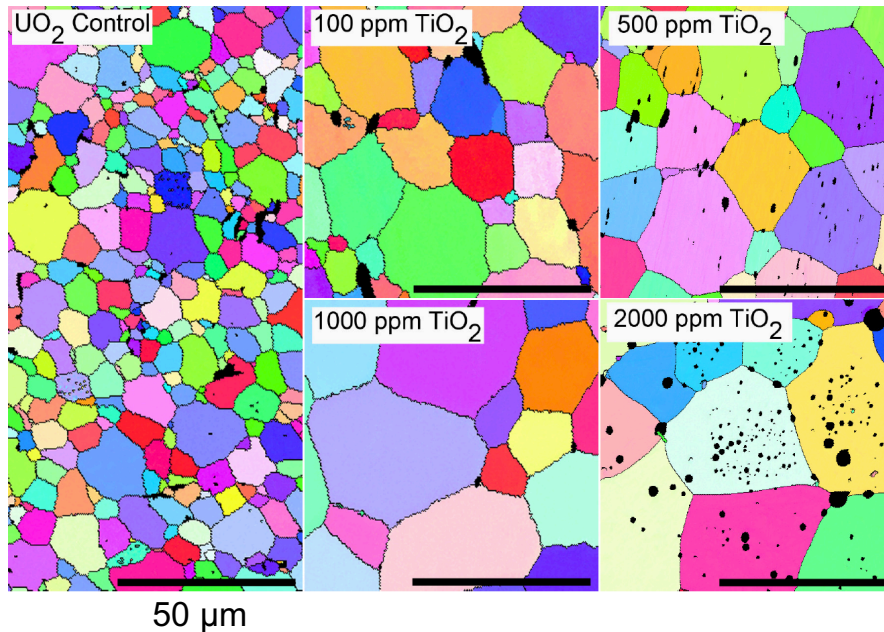
More than 1 *d* electron  
so 2+ is an option

s2 2+		s2d										s2p1 3+										He 2
H 1	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10				
Na 11	Mg 12	Al 13											Si 14	P 15	S 16	Cl 17	Ar 18					
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36					
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54					
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86					
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118					
			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71						
			Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103						

- Comparison of Cr and Al highlights importance of 2+ valence state for interstitial
- Other possibilities are group 2 elements or transition metals with more than 1 *d* electron
- Expect transition metals with low monoxide stability to be more effective
- C, Si and N are excluded due to formation of secondary phases

# Other d elements: Ti

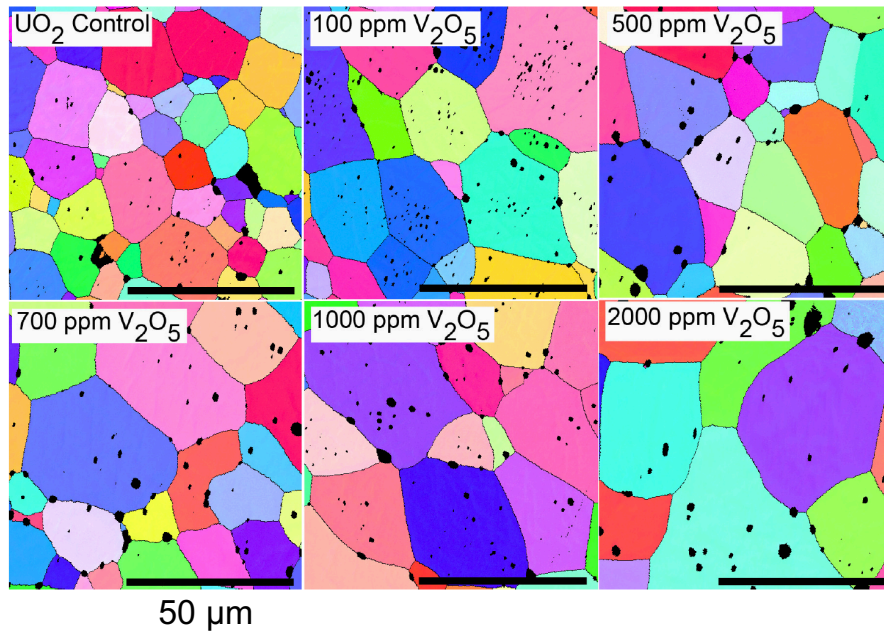
Nelson *et al.* LANL Tech Rep, M3FT-13LA020206



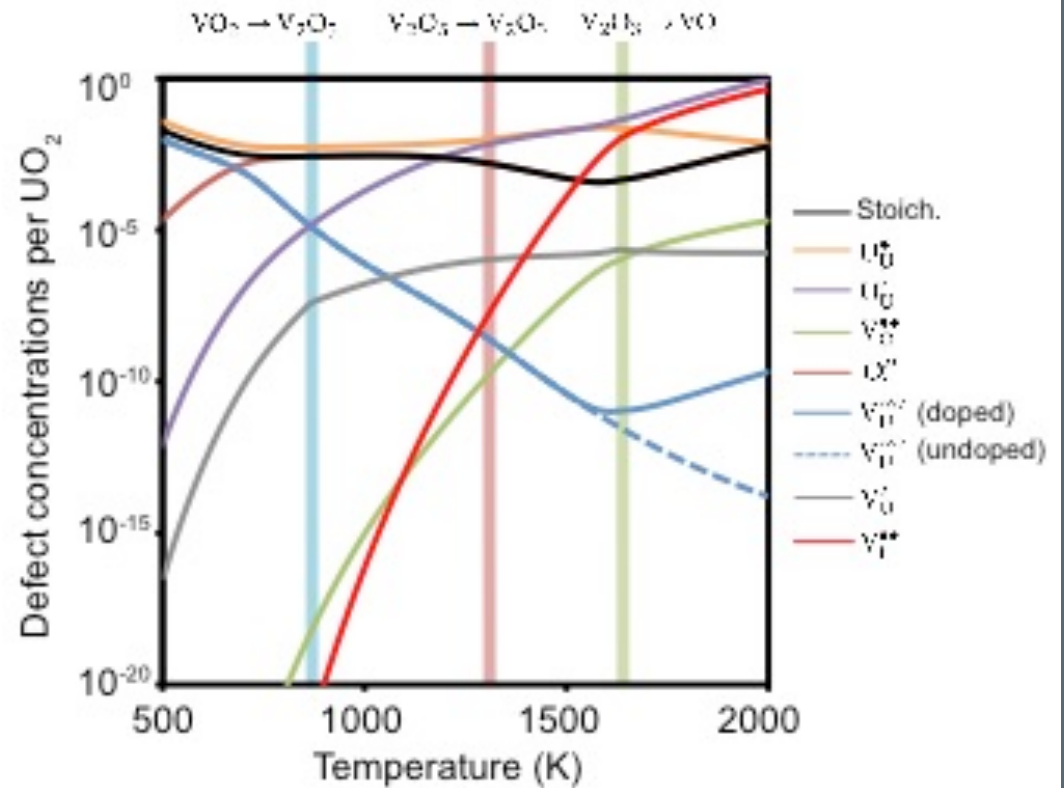
- Agreement with past work at LANL that Ti should enhance grain size
- Anecdotally: Ti leads to non-uniform grain size.

# Other d elements: V

Nelson *et al.* LANL Tech Rep, M3FT-13LA020206

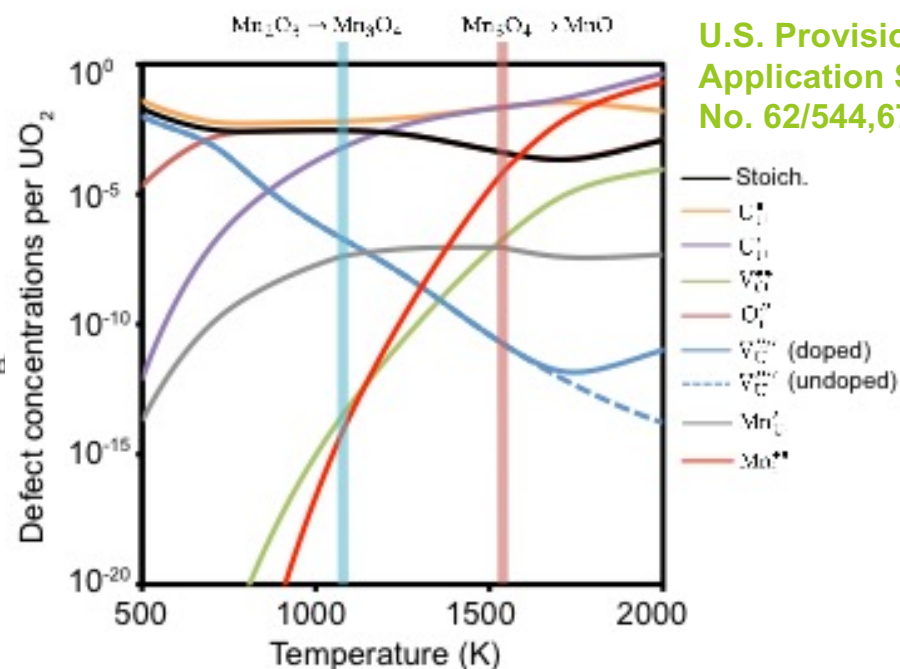
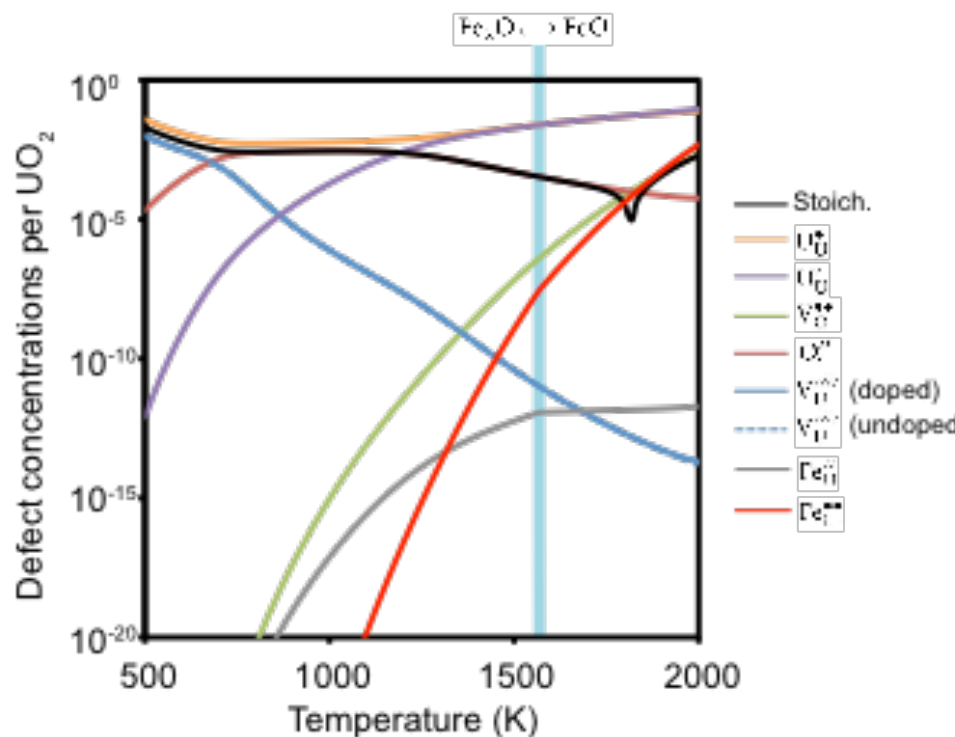


- Agreement with past work at LANL that V should enhance grain size



# Untested (i.e. unpatented) d elements:

## *Fe and Mn*



U.S. Provisional  
Application Serial  
No. 62/544,673

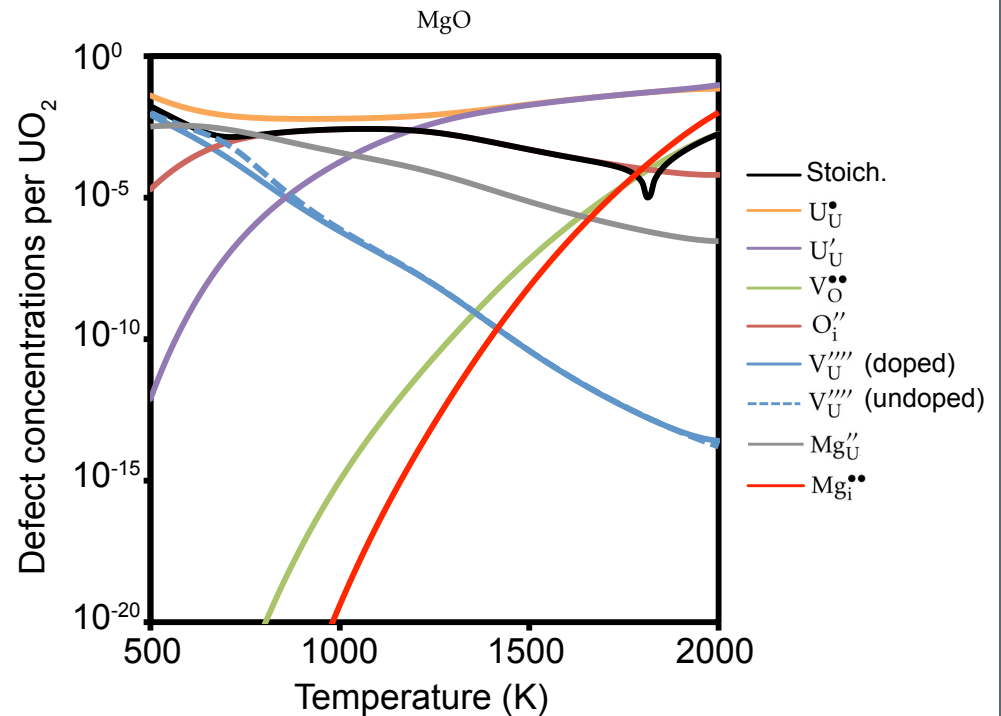
❑ Fe does not have a significant impact. However...

❑ Mn enhances  $\text{V}_\text{U}$  concentrations and therefore grain size. Not known until now.

*Patent filed for  
“Mn-doped oxide nuclear fuel” on 11<sup>th</sup> August*

## Group 2: Mg-doped $\text{UO}_2$

- ❑ Marginal increase in  $V_U$  at high temperatures
- ❑ Significant solution at substitutional site at low temperatures
- ❑ Experimental work [1] showed that Mg can be accommodated either interstitially or substitutionally
- ❑ In experimental work high temperature favored the interstitial site
- ❑ This agreement provides further support for the proposed interstitial mechanism of enhanced doping
- ❑ Not as effective as  $d$  electron dopant due to the stability of MgO compared to CrO, MnO etc.

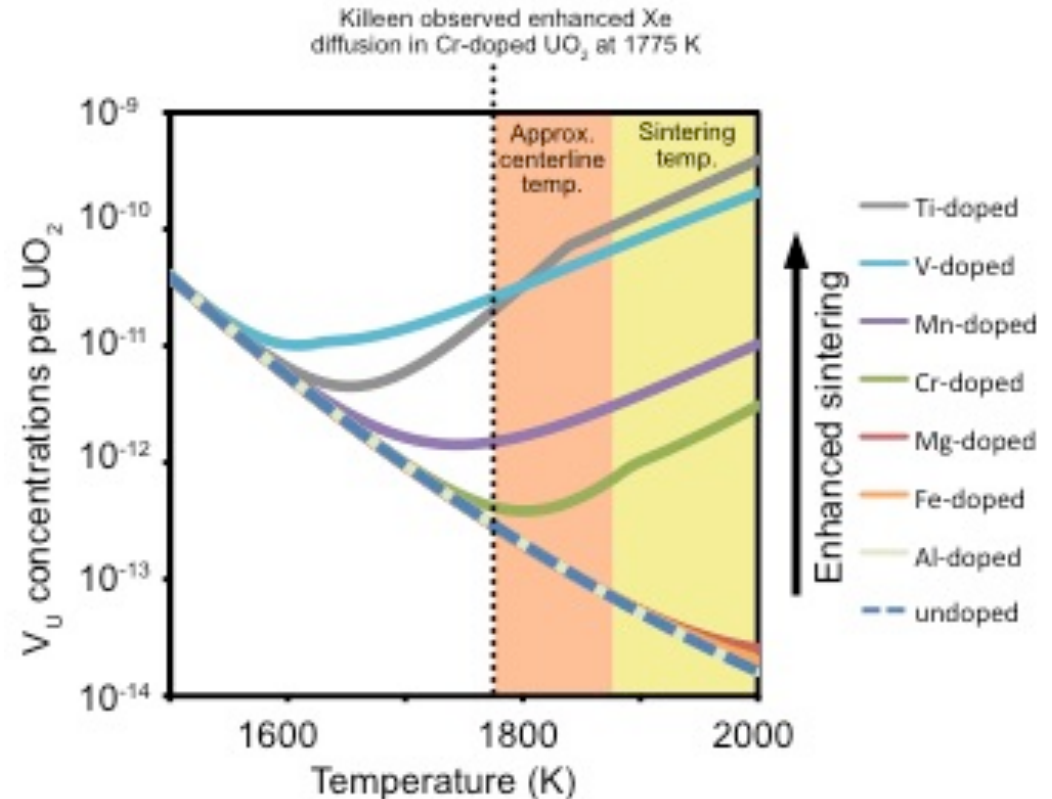


[1] Fujino *et al. J. Nucl. Mater.* **246** 150-157 (1997)



# Conclusions

- ❑ Modeling these systems accurately requires no assumptions regarding the possible valence states of dopant or actinide metals
- ❑ Vibrational entropy is decisively important at high temperatures for sintering
- ❑ A common 2+ interstitial mechanism is identified for small transition metal dopants and Mg (group 2)
- ❑ Al could not readily form the 2+ interstitial due to lack of d electrons → low solubility
- ❑ Good agreement with experiment about which dopants enhance grain size
- ❑ Mn identified for first time and a patent has been filed for “Mn-doped oxide nuclear fuel” **U.S. Provisional Application Serial No. 62/544,673**



# Future Work:

## MARMOT-BISON Fission Gas Study

Killeen, JNM 88 (1980) 177.

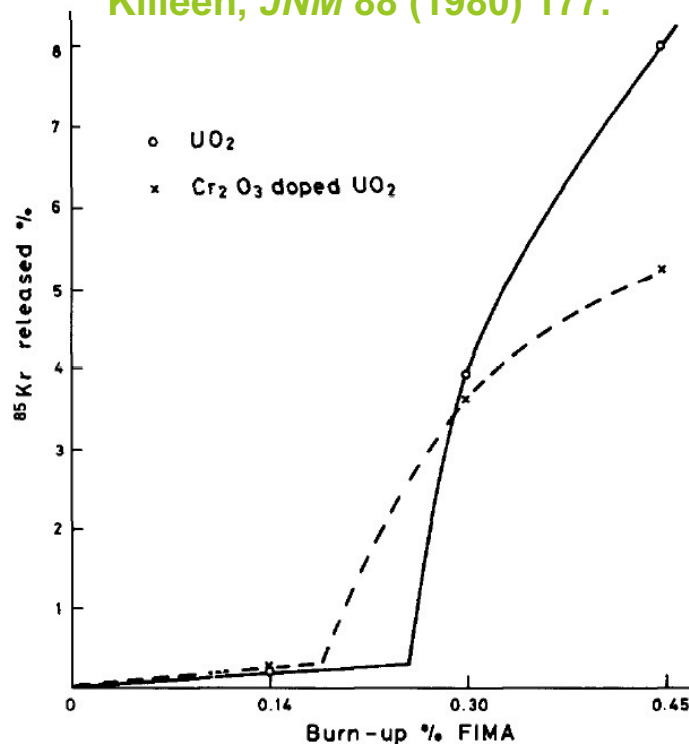
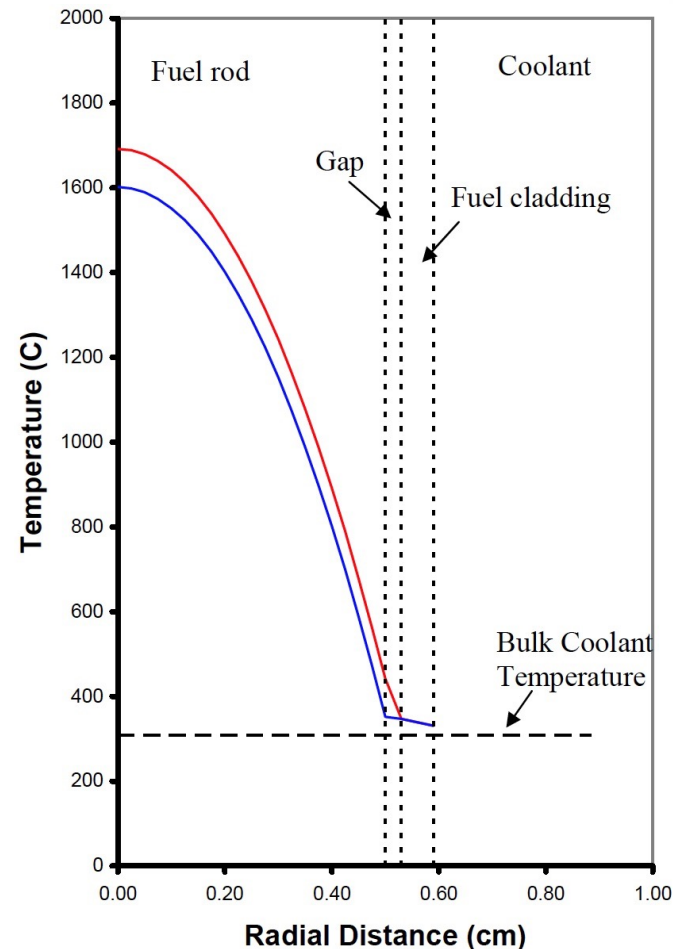


Fig. 2. Plot of gas release against burn-up. The curves are plotted from eq. (2) for the undoped samples and eq. (4) for the doped samples. The release values shown here have been corrected as described in the text to allow for evaporation loss and temperature differences between the samples.

$$D^{\text{UO}_2} (1465^\circ\text{C}) = 1.3 \times 10^{-20} \text{ m}^2/\text{s},$$

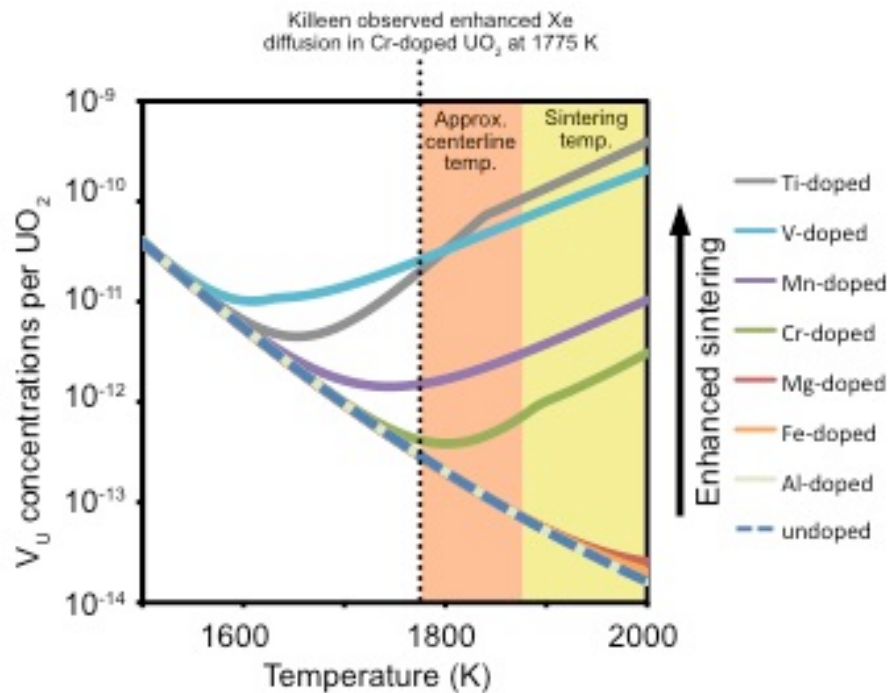
$$D^{\text{Cr}_2\text{O}_3} (1500^\circ\text{C}) = 7.9 \times 10^{-20} \text{ m}^2/\text{s},$$



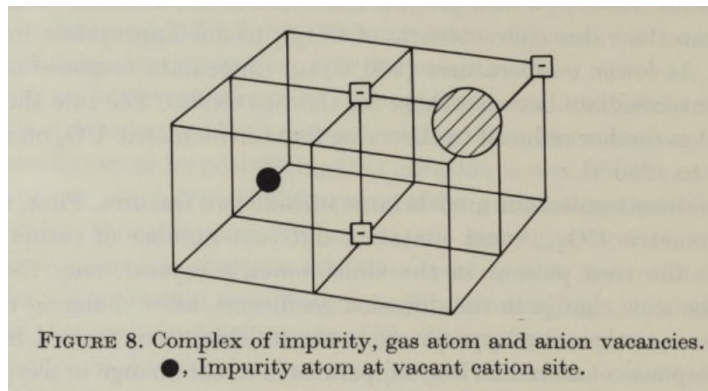
From Olander and Motta

# Future Work:

## *MARMOT-BISON Fission Gas Study*



Factor ~5 difference in  $D$  (from Killeen experiment) corresponds to factor ~5 difference in uranium vacancy concentration at same  $T$ .



CRA Catlow, *Proc Roy Soc A* **364** (1978) 473.

Previous explanation (large cluster D) clearly inaccurate.

**MARMOT-BISON calcs of enhanced  $D$  (~5x) vs larger grains (also ~5x) will be of great interest to vendors and NRC**



# Comparison to Areva Studies?

## Behavioral Assessment

Ioan Arimescu  
AREVA Senior Expert

## Fission Gas Release

- ▶ Larger grain size means longer diffusion paths to grain boundaries and thus delayed fission gas venting to open voidage
- ▶ Also, increased intragranular porosity with more gas retention inside the grains
- ▶ However, measured fission gas release is not reduced to the extent corresponding to the increased grain size. Heterovalent cation dopants, such as Cr, affects the lattice defect concentration equilibrium, which impacts the diffusion process of Uranium and gas atoms.

» Fuel code fission gas release model is applied for larger grain doped-fuel with re-calibrated gas atom effective diffusion coefficient

# Future Work:

## *MARMOT-BISON Fission Gas Study*

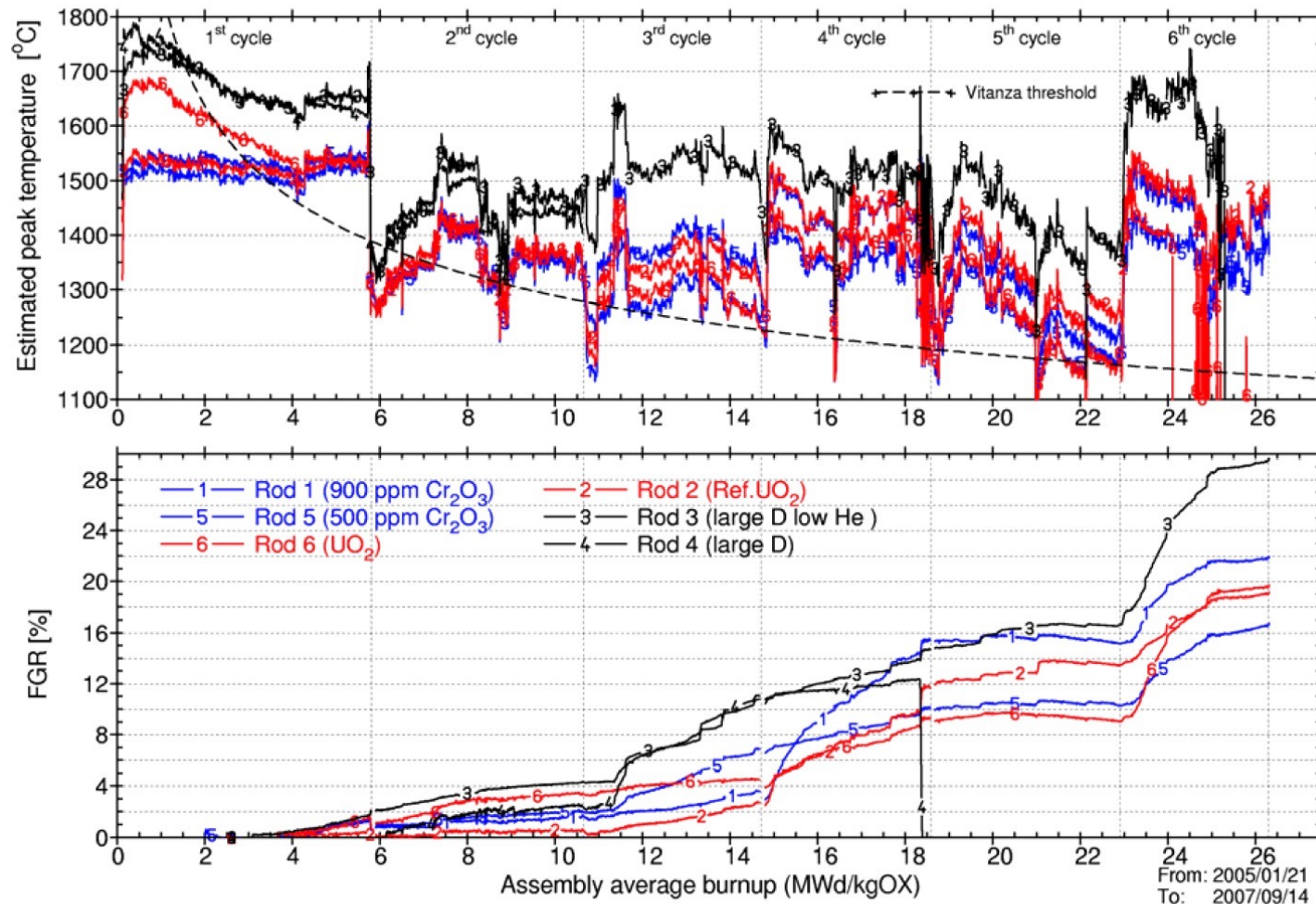


Figure 39 - Estimated fission gas release fractions.

From Josek, THE HIGH INITIAL RATING TEST IFA-677.1: FINAL REPORT ON IN-PILE RESULTS (2008)